

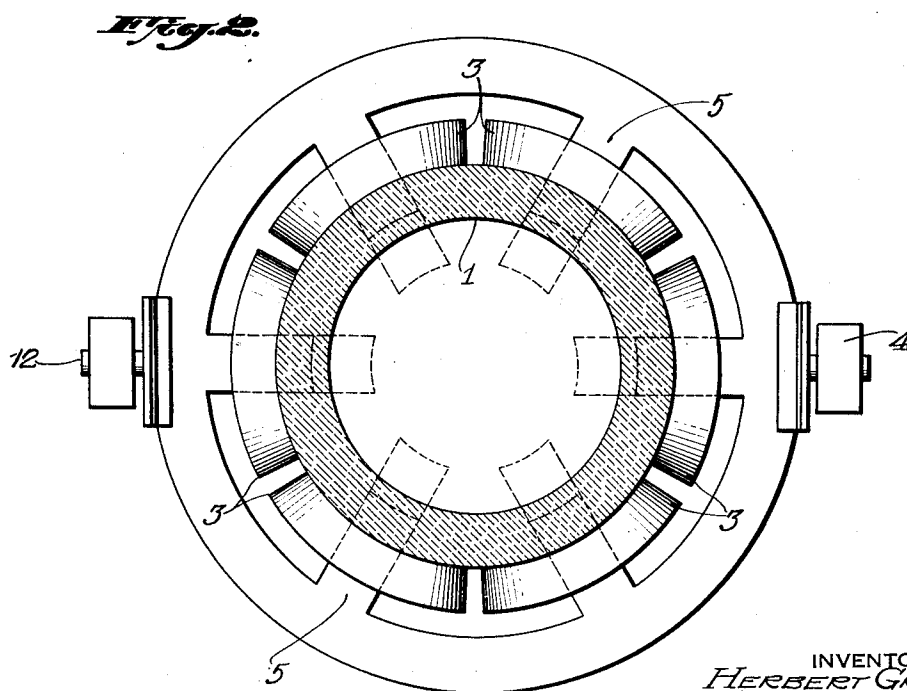
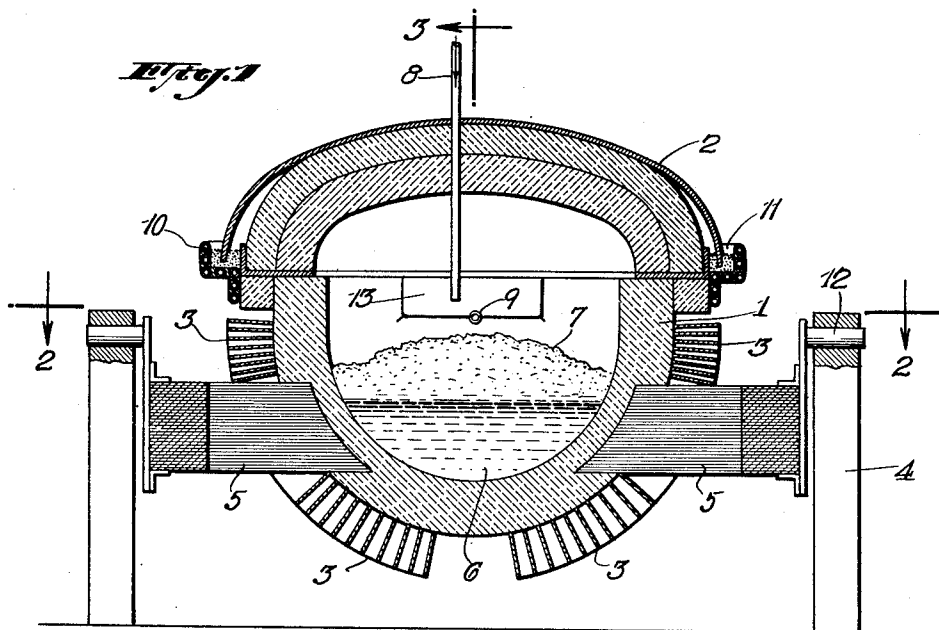
May 19, 1936.

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2,041,333

APPARATUS FOR PRODUCING CARBON FREE METALS, ALLOYS AND THE LIKE

Original Filed April 9, 1932 3 Sheets-Sheet 1



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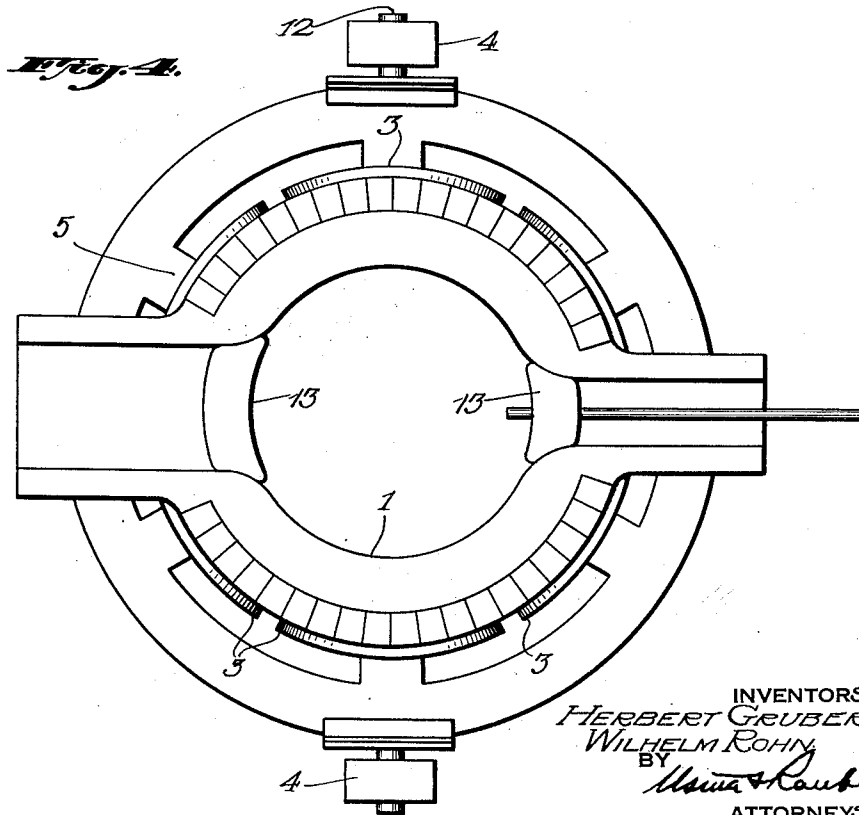
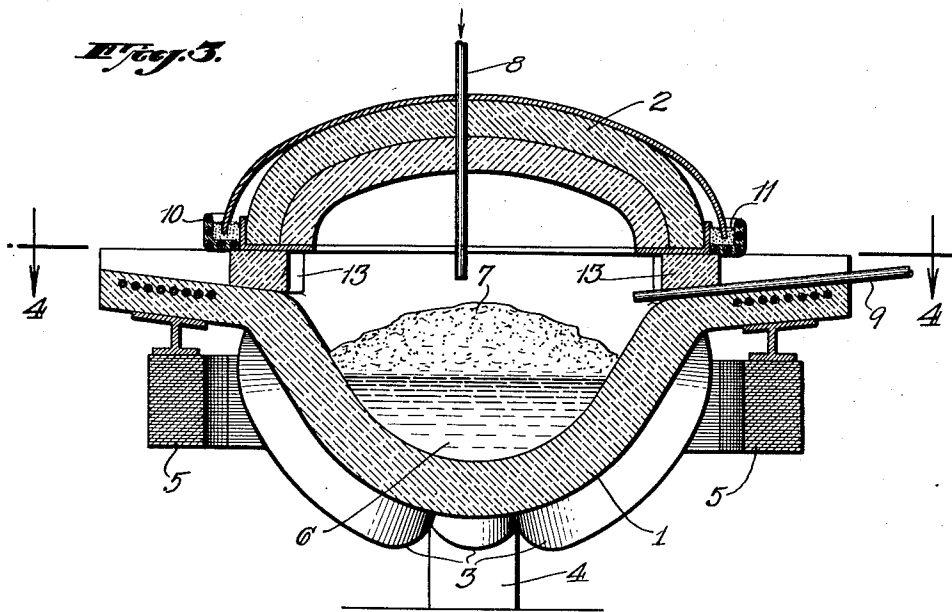
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APPARATUS FOR PRODUCING CARBON FREE METALS, ALLOYS AND THE LIKE

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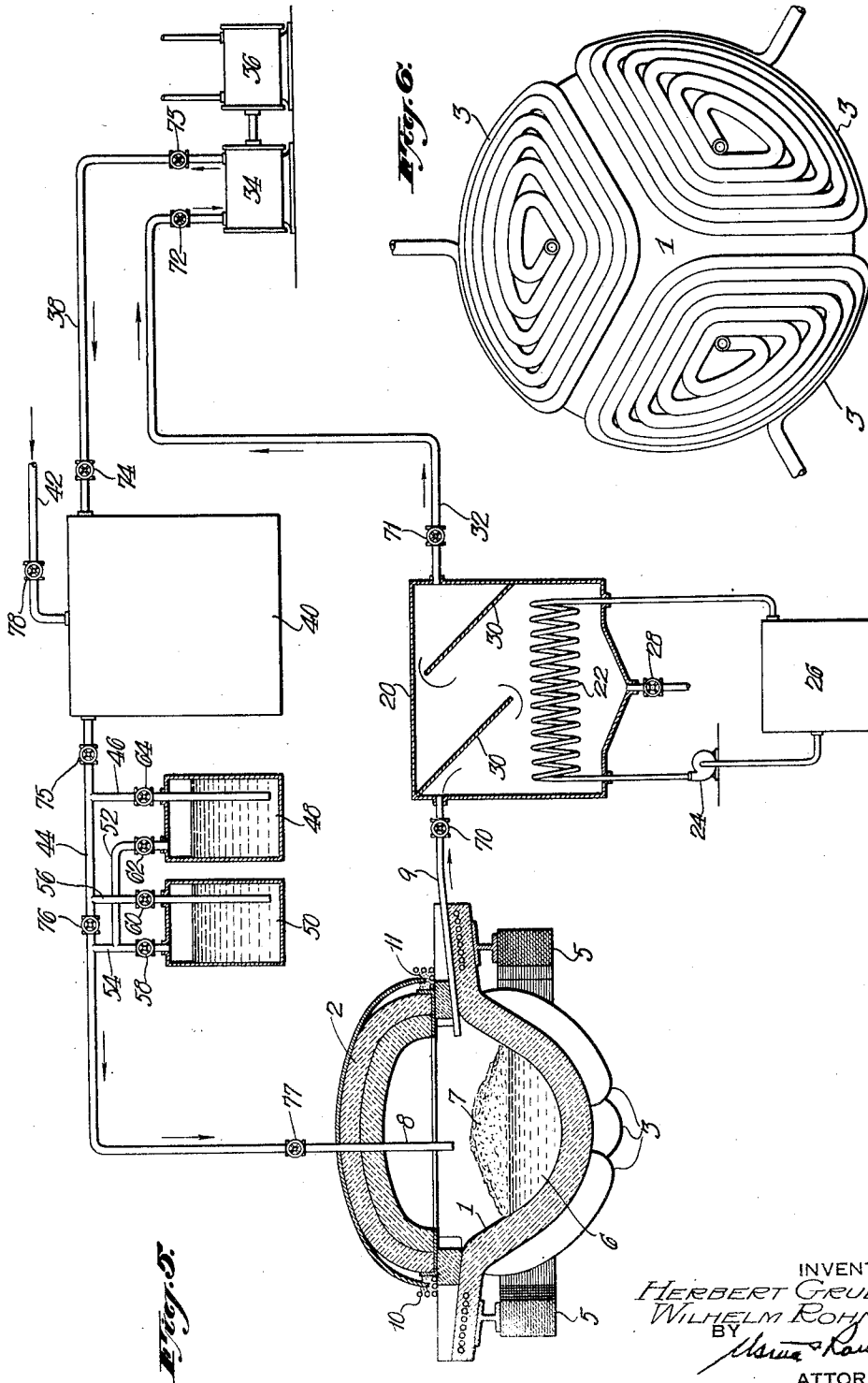
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UNITED STATES PATENT OFFICE

2,041,333

APPARATUS FOR PRODUCING CARBON-FREE METALS, ALLOYS, AND THE LIKE

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Original application April 9, 1932, Serial No. 604,315. Divided and this application August 8, 1933, Serial No. 684,258

4 Claims. (Cl. 13—26)

This invention relates to metallurgy and to apparatus for producing substantially or approximately carbon-free alloys, ferro-alloys, steels and the like, and is a divisional application of application Serial No. 604,315, filed April 9, 1932, entitled Method of Producing carbon-free metals, alloys and the like.

The exhaustive studies as to the use of stainless (corrosion-resisting) steel have shown lately that for all purposes in connection with which the material fact is not the cutting hardness, but primarily the resistance to corrosion, it is desirable to make the carbon content of such stainless steel as near to zero as possible, but at most less than 0.05%. Such a low carbon content is of special importance in all cases in which parts of apparatus are united together by welding, for the reason that near the welding seam easily intensified corrosions can occur if it is not possible, after welding to subject the welded object or apparatus to a refining heat treatment in order to bring the entire carbon content of the steel into an innocuous dissolved form. The same annealing step must be applied where the shaped or fabricated pieces are subjected to deformation while cooling or cold.

For the manufacture of ferro-chromium which is extremely low in carbon, and also for the manufacture of stainless steel extremely low in carbon, a number of processes have heretofore been suggested. The oldest process starts from carbon containing ferro-chromium or chrome steel and endeavors to refine out the carbon by oxidizing treatment with air or other agents which give off oxygen such as metallic oxides or ores; this method can be easily carried out in induction-melting furnaces, in which the well known eddying bath movement made the reaction more uniform, accelerated and perfected it. However, it is extremely difficult to reduce the carbon content in this manner in ferro-chromium below about 0.2–0.3% and in chrome steel below about 0.08–0.12%. At these low carbon contents there occurred in the product noticeable quantities of oxides which, in their turn, also had an injurious effect on the corrosion resistance. Therefore, the suggestion was made to make this process more complete in the manner that it is carried out under reduced pressure in order to be able by the reduction of the partial pressure of the carbon monoxide occurring as reaction product, to make the reaction as complete as possible and to avoid the occurrence of oxides as far as possible. The results of this manner of procedure are satisfactory, if the proper apparatus is selected, but the

process is complicated and very expensive on account of the necessity of operating in a vacuum furnace.

In a copending application Serial No. 589,526, filed January 28, 1932, now issued as United States Patent No. 1,906,184, a process is disclosed adapted to produce substantially or approximately carbon-free chrome steels and ferro-chromium which contemplates the introduction of chromium into a liquid and possibly superheated iron bath by the reduction of chromic oxide or chrome ore with hydrogen. The reduction of chromium oxide by hydrogen is considerably facilitated and accelerated in the presence of a metal serving as a "receiver" or "absorber" for the reduced chromium. This process gives excellent results and is advantageous for the manufacture of chrome steels of up to 20–30% chrome content with hydrogen of what is known as commercial grade of purity. Where it is desired to obtain a higher chrome content in the alloy the hydrogen used for the reduction must be freed from traces of steam (water vapor) to such a far reaching extent, as is not very easy in connection with the manufacture thereof on a large scale, and, in particular, it can only be achieved at comparatively high cost.

In a second copending application Serial No. 604,314, filed April 9, 1932, now issued as United States Patent No. 1,915,243, a process is disclosed for preparing substantially pure chromium by the reduction of chromium oxides with hydrogen at temperatures in excess of about 1750° C., the hydrogen having previously been freed from water vapor by exposure to temperatures between –60° to –70°.

We have found that in the removal of the carbon from a carbon-containing ferro-chrome or chrome steel by the prior art oxidizing action can be made more effective and also is considerably accelerated, if carried out in a hydrogen atmosphere rather than under purely oxidizing conditions as heretofore practiced. Whereas, for instance, in a high frequency furnace as a result of a reaction of a 60% ferro-chromium (containing 4–6% carbon) with air or chromic oxide or chrome ore after 3 hours reaction time, one obtains a final product which still contains about 0.2–0.15% carbon and which at the same time shows an inadmissibly high oxide content one obtains under absolutely identical conditions, but in a hydrogen atmosphere, only after 1½ hours, a product with less than 0.05% carbon. If chromic oxide is used as oxidation agent, the chrome content of the alloy also is increased from the original 60% to about 65%.

In accordance with the present invention a ferro-chromium or chrome steel containing more or less carbon, obtained in the customary manner, can be treated in a hydrogen atmosphere with excess oxide or ore of a metal, which, in itself is to form a constituent of the alloy to produce a ferro-chromium or chrome steel low in carbon. The metal oxide used in this decarburizing process may be comprised, if a nickel containing stainless carbon-free chrome steel is to be produced of nickel oxide or of nickel oxide admixed with iron and/or chromium oxides. Iron oxide or chromium oxide alone may be used, if desired. In the melting of the metal bath inductive heating means is preferred, and especially low frequency inductive heating because of its more effective stirring effect.

In a third copending application entitled Induction furnaces, filed August 15, 1931, bearing Serial No. 557,234, issued as U. S. Patent No. 1,983,242, Dec. 4, 1934, one of the applicants has disclosed a novel type of induction furnace operable by a three phase electric current in which each phase of the three phase current flows through one single coil or a group of coils. Owing to the action of the three phase current a rotation of the entire molten metal bath takes place around a vertical axis. On this movement is superposed another movement which takes place in front of each single phase energized coil and which consists in a rotation about an axis which is perpendicular to the plane tangent to each coil at its center. When the melting hearth is hemispheroidal these axes of rotation in front of the coils are slightly inclined upward when regarded from the outside to the inside. This type of stirring may be made relatively vehement by suitable regulation of the current strength and the number of coils and the like factors as is more fully disclosed in the said copending application. This type of inductive heating and stirring is particularly adapted to be utilized in the practice of the present invention, inasmuch as it assures that all parts of the molten metal bath are rapidly brought to the surface into contact with the hydrogen and with the metal oxides thus facilitating and accelerating the decarburizing reaction and the absorption of the reduced metal within the metal bath, and facilitating the oxidation of the carbon contained in the metal bath with the metal oxides introduced therein or any oxidation agent comprised within the hydrogen atmosphere.

In the accompanying drawings we have illustrated apparatus useful for the purposes of the present invention. Referring to the drawings,

Fig. 1 is a sectional side elevational view of a type of apparatus suitable for the purposes of the present invention;

Fig. 2 is a top view of the same partly in section along plane 2—2, Fig. 1;

Fig. 3 is a sectional side elevational view along plane 3—3 of Fig. 1;

Fig. 4 is a top view of the same with the cover removed as indicated along plane 4—4 of Fig. 3;

Fig. 5 is a view partly in schematic detail of the furnace of Figs. 1 to 4 inclusive cooperatively assembled with suitable gas purification apparatus; and

Fig. 6 is a bottom plan view of the furnace illustrating the details of the special type electric induction coils utilized therein.

Referring to the drawings, the furnace of Figs. 1 to 4 inclusive includes a pot-shaped container interiorly lined with suitable refractory materials, a top 2 adapted to be hermetically sealed

on the container as indicated at 11 and preferably the seal should be water cooled as indicated at 10.

About the container 1 are positioned a plurality of electric induction coils 3 which coils are preferably dish-shaped as indicated to fit the contour of the container 1 substantially as disclosed and claimed in the copending application No. 557,234 above identified. These coils 3, yoke 5 and container 1 are cooperatively assembled and supported rotatably by rotatable pins 12 positioned in opposite sides of the container recessed in bearing openings of supports 4.

Within the container 1 is a molten bath 6 and superposed thereon is metal oxide 7. Through the top section of top 2 passes pipe 8 through which hydrogen is introduced and through one of the pouring outlets of container 1, normally closed by plugs 13 extends outlet pipe 9.

As the practice of the present invention requires the maintenance of a strong free flow of hydrogen through the container over the metal oxides 7 superposed upon the metal bath 6, it is essential that means be provided to supply hydrogen to the container and to constantly regenerate the hydrogen exhausted from the container for return to the circuit. This means is illustrated in Fig. 5. The hydrogen for the present invention is stored under pressure in tank 40 from which it passes through valves 75, 76 and 77 and appropriate piping to pipe 8. The spent hydrogen effluent through pipe 9 is carried through valve 70 into cooling chamber 20 wherein by means of suitable baffles 30 it is passed over freezing coils 22 wherein the moisture content thereof is removed. Freezing coils 22 should preferably contain fluid or gases cooled to temperatures approximating -60° to -70° C. substantially as disclosed in my copending application No. 589,526 now issued as United States Patent No. 1,906,184 above identified. This fluid or gas may be circulated therethrough from refrigerator means 26 by pump 24 substantially as indicated.

The hydrogen free from water vapor then passes through valves 71 and 72 and appropriate piping to compressor pump 34 driven by motor 36 and thence through valves 73 and 74 and appropriate piping back to storage tank 40. Means such as indicated by pipe 42 and valve 78 are provided to permit additions of hydrogen to the tank 40 as the same is used up and removed as water vapor. Means 28 are provided in the bottom of chamber 20 to periodically remove the water vapor collected therein.

Alternatively a mixture of carbon and metal oxide (chrome ore) may be used, the quantity of carbon used being adapted to just suffice to reduce the oxides present and to effect the reaction in the hydrogen atmosphere; a deficiency of carbon may be used if desired, leaving a certain part of the oxides unreduced which may be added to the next charge, or the oxides remaining after the carbon is used up may be reduced by the hydrogen. Another alternative comprises adding carbon and chromic oxide or chrome ore, either simultaneously or successively, in suitable quantities to a liquid metal bath in a hydrogen atmosphere.

The present invention is especially advantageous for the remelting of chrome steel scrap in which the oxides naturally existing on the surface of the scrap or intentionally added oxides or ores may be utilized to bring down the carbon content of the alloy nearly to zero in a hydrogen atmosphere, without having to contend, on the

other hand with an undesirably large oxide content of the finished steel.

Likewise, the present invention is valuable in the production of carbon-free chrome steel, even in those cases in which one starts with an iron bath which is as free as possible from carbon, intending to dissolve in same a ferro-chrome which is as free as possible from carbon. As is well known, it is extremely difficult to decarburize an iron bath in accordance with prior practices to less than about 0.04% carbon, without, at the same time, increasing the oxygen content to a deleterious amount. If, on the other hand, this decarburizing process is carried out in a hydrogen atmosphere, then one can either start with an iron bath with a somewhat higher carbon content, and completely eliminate the carbon content of same in a dependable manner, or as above disclosed the hydrogen atmosphere may be utilized on an already superfined or low carbon but oxygen containing iron bath to eliminate in a dependable manner the oxides contained therein. Other types of steels may of course be similarly treated, for purposes in which thorough deoxidation, either alone or together with controlled decarburization is essential.

It is also possible to modify the hydrogen atmosphere in such a manner that it acts as a mild slightly oxidizing agent, as by introducing a sufficient, controlled amount of water vapor or other oxygen carrier before the hydrogen is passed into the reaction chamber. By this means the carbon may be removed from the metal without oxidizing the chromium. The oxygen content of the hydrogen required for this purpose must be selected in a higher or lower percentage depending on the chromium or other alloy content of the product. On the other hand the normal reducing action of the hydrogen may be facilitated by incorporating therein an appropriate proportion of a vaporizable hydrocarbon such as benzol, light petroleum, distillates, natural gas and the like. Chromium oxides or a chrome ore may be subjected to the hydrocarbon-containing hydrogen in the presence of a liquid metal bath as heretofore disclosed, the reducing reaction being facilitated by the hydrocarbon vapor in the hydrogen. If desired, a relatively small bath of molten metal may be employed. The carbon content of the hydrogen should be regulated or adjusted to be such that no carbon from it remains in the final product.

To permit this we provide means as illustrated in Fig. 5 to introduce alternatively water vapor or hydrocarbon vapor in the gas stream flowing to furnace 1. This means comprises containers 48 and 50 in one of which is water and in the other a volatile hydrocarbon such as benzol. By closing or partially closing valve 76 and opening or partially opening either of the valve combinations 60 and 58 or 64 and 62, any desired proportionate admixture of water vapor or hydrocarbon vapor can be introduced within the hydrogen gas stream flowing to furnace 1.

We have also found that appropriate mixtures of fuel gases such as water gas, coke oven gas or other gases made from coal may also be used as mild oxidizing agents or as reducing agents for the processes outlined above.

One novel feature of the present invention resides in the fact that the entire process may take place at normal pressures and that therefore, all the packings only need to withstand very small pressure differences. It is therefore pos-

sible to start the furnace completely open to the air and after charging the reacting substances to produce the hydrogen atmosphere directly or indirectly for instance by placing over the entire furnace a light-weight hood filled with hydrogen which may possibly fit into an oil groove or a sand seal at the level of the top of the furnace. After termination of the process this hood can again be removed and the furnace is thereupon again completely open and accessible for the casting of the charge into ingots, without hindrance from any structural parts which would be necessary for the application of an increased or reduced pressure. On the other hand, it is also possible to make this hood pressure-proof and to connect it in a pressure-proof manner with a counter-flange attached to the furnace, in order to be able to carry out the entire process under increased pressure for further acceleration.

The hydrogen may be removed at a suitable place and be again brought in to the reaction zone after suitable elimination of the reaction products. When a mixture containing water gas and/or coke oven gas is used, the residue may be applied as a fuel gas.

While as a specific embodiment of the practice of the present invention reference has been made to the production of carbon-free chromium and to the manufacture of carbon-free ferro-chromium and chrome steels it is not to be construed as being limited thereby. The present invention can also be applied in an absolutely analogous manner for the production of other alloys, ferro-alloys, steels and the like, such as ferro-tungsten, ferro-molybdenum, ferro-uranium, ferro-vanadium, ferro-zirconium, ferro-titanium, chrome steels, chrome-molybdenum, chrome-nickel steels and for the production of ternary or quaternary alloyed steels.

Furthermore, in this way, there can be produced substantially pure metals and also alloys of the said elements, chromium, molybdenum, tungsten, uranium, vanadium, zirconium and titanium with each other and with other basic substances than iron, such as nickel, cobalt, copper and/or other metals.

Having broadly and specifically disclosed the present invention it is apparent that many modifications and adaptations may be made therein without departing essentially from the nature and scope thereof as may be set forth in the following claims:

What we claim is:

1. In combination, a hearth, a molten metal bath on said hearth, means to heat said bath by induced electric currents said means being adapted to induce vigorous circulation in said bath to recurrently bring all portions of the bath to the surface thereof, a cover enclosing the hearth and the surface of said bath from the atmosphere, inlet and outlet openings in the cover, means to supply a pressure of reducing gas through said inlet opening and means to conduct the gas effluent from said outlet opening through a gas purifying system and to return the purified gas to said inlet opening.

2. In the combination of claim 1, said gas purifying system including means to remove water vapor from said gas.

3. In combination, a hearth, a molten metal bath on said hearth, means to heat said bath by induced electric currents said means being adapted to circulate the said bath in a plurality

of radially vertical rotating planes as well as horizontally, a cover enclosing the hearth and the surface of said bath from the atmosphere, inlet and outlet openings in said cover, a source
5 of substantially pure dry hydrogen, means to conduct a pressure of said hydrogen into the cover through said inlet opening, and means to conduct the effluent gas from the said outlet opening through a gas purifying system adapted to

remove water vapor from the said gas and to return the purified gas to the said source.

4. In the combination of claim 3, means to introduce in said pressure of hydrogen before entering said cover a proportion of other gases
5 selectively reactive with undesired constituents of the bath to form gaseous products therewith.

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